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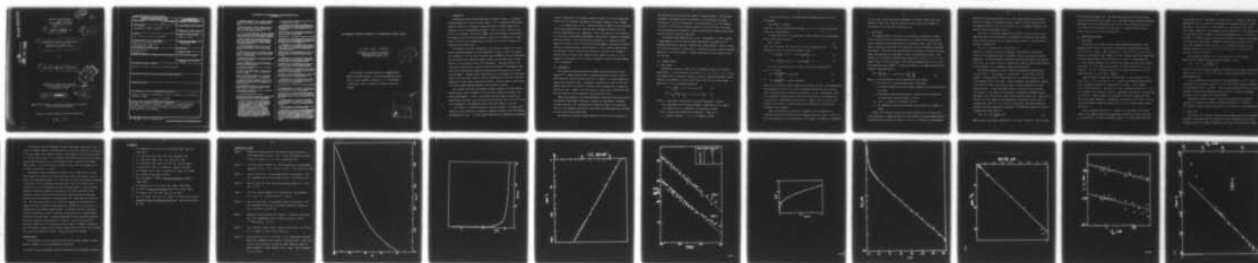JAN 78   J E LEWIS, A L RHEINGOLD   N00014-75-C-0798

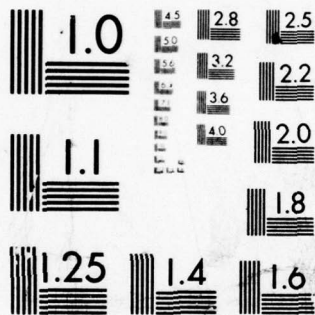UNCLASSIFIED   TR-10   NL

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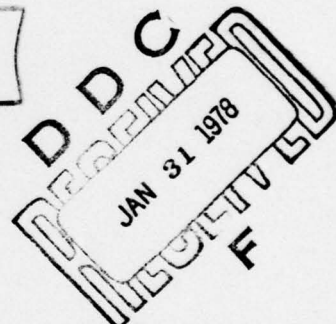
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(6) LOW FREQUENCY DIELECTRIC RESPONSE OF AN

ORGANOARSENIC POLYMER $(CH_3As)_x$.

By

(10) John E. Lewis and Arnold L. Rheingold

State Univ Coll.,
Departments of Physics and Chemistry
State University of New York
Plattsburgh, NY 12901

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The dielectric relaxation behavior of bis[catena-poly(methylarsenic)], $(CH_3As)_x$ at excitation frequencies below 10 Hz is highly anomalous, varying as ω^{-9} This behavior is examined in terms of Jonscher's 'universal' dielectric response.

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LOW FREQUENCY DIELECTRIC RESPONSE OF AN ORGANOARSENIC POLYMER $(CH_3As)_x$

J. E. Lewis and A. L. Rheingold

Departments of Physics and Chemistry
State University of New York
Plattsburgh, NY 12901, U.S.A.
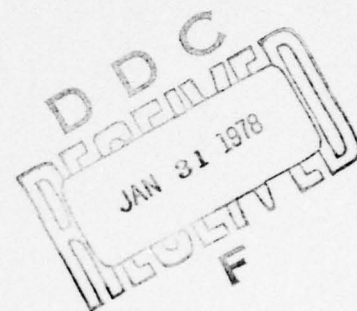
The dielectric relaxation behavior of bis[catena-poly (methylarsenic)], $(CH_3As)_x$, at excitation frequencies below 10 Hz is highly anomalous, varying as $\omega^{-.9}$. This behavior is examined in terms of Jonscher's 'universal' dielectric response.

I. INTRODUCTION

Bis [catena-poly(methylarsenic)], empirical formula $(CH_3As)_x$, is the first-discovered member of a novel structural type[1]. It is a crystalline organoarsenic "polymer" formed by the stacking of $CH_3As-AsCH_3$ units in ladder fashion as determined by x-ray crystallographic analysis[2]. The a.c. and d.c. electrical properties of the polymer, herein called BCPMA, have been described in some detail[3]. The imaginary part of the sample impedance, which can be interpreted as a capacitance, was found to vary approximately inversely with excitation frequency, for frequencies below about 10 Hz.

This behavior is usually considered to be extrinsic in nature, due to interfacial electrode phenomena, but other experimental evidence, notably the exponential dependence of the dielectric relaxation time of BCPMA with inverse temperature and the frequency and temperature ranges in which the loss peak occurs, is more indicative of an intrinsic origin of the phenomenon. Such high dielectric constant effects were initially reported by Pohl and coworkers[4-6] who suggested that a new type of polarization mechanism, hyperelectronic polarization, was present in their samples. Hyperelectronic polarization may be considered due to the interaction (with the external electric field) of charged pairs of excitons, localized temporarily on long, highly polarizable molecules. Thus the effect is most likely to be seen in semi-conducting materials with extended structures.

More recently this same low frequency dielectric behavior has been found in materials whose carrier transport is via electronic hopping--the amorphous and glassy semiconductors. In fact, such behavior has been termed 'universal' by Jonscher[7] who gives long lists of diverse solid dielectrics that vary as ω^{n-1} (n<1) at low frequencies, from spattered films of lead-zinc-niobate to dry sand.

In an effort to clarify the dielectric response of BCPMA, a long-chain semiconductor, we have studied its response to transient voltages of the step-function and ramp-function type. It is well known[8] that the use of charging and discharging

currents yields data for the complex dielectric constant at very low frequencies, below 10 Hz, the frequency range where the dielectric anomaly is seen in BCPMA.

It is noteworthy that the a.c. conduction process in BCPMA has been determined to be carrier hopping between localized sites, although the material is an intrinsic semiconductor at d.c. frequencies. This is the same a.c. carrier process as in the glassy and amorphous semiconductors where similar anomalous low-frequency dielectric behavior can be inferred from low-frequency a.c. conductivity data[7]. However the system in which Pohl observed the most dramatic hyperelectronic polarizability, a polyacene quinone radical polymer[6], is also a planar ladder polymer. In the present system, extensive electron delocalization must occur through d-orbital centers on arsenic; that these d-orbital centers can result in a "conjugated" system similar to the π-electron conjugation in Pohl's polyacene polymer is not unreasonable.

II. EXPERIMENTAL

The synthesis and characterization of BCPMA has been described in several reports[1-3,9]. BCPMA typically forms in irregular crystallite clusters of millimeter dimensions, which precludes fabrication of samples to the usual geometrical shapes used in dielectric work. Consequently, gold wires of 0.005-in (0.127 mm) diameter were directly attached to selected crystals of BCPMA using a commercial silver-epoxy glue. Contacts were then baked for several hours at 60°C after which they were found to be both mechanically and electrically sound.

Samples were housed in a variable-temperature, light-tight shielded enclosure, Cu-Constantan thermocouples being used to measure the temperature. Particular attention was paid to the interconnections between the sample and the measuring circuit, as the impedance involved were quite high, introducing problems associated with noise and system response time.

The sample was excited by voltage transients of either the step-function or

the ramp-function type from a Wavetek model 114 signal generator. The resulting charging or discharging current was measured by a Keithley model 615 digital electrometer in its fast response mode. The electrometer has an input impedance in excess of 10^{14} ohm and can measure currents as low as 10^{-14} amp. The output of the electrometer was displayed on either a chart recorder (Honeywell model 196) or an oscilloscope (Tektronix model 556).

The maximum voltage employed was 32 volts, corresponding to a field strength of approximately 1000 Vcm^{-1} and the longest time interval considered for the transient waveforms was 1000 sec, limited by the signal generator. Times in excess of 10^4 sec were required to obtain the d.c. steady-state current through the samples, especially at the lower voltages. A highly regulated d.c. power supply was used for this task.

III. GENERAL THEORY

A. Step Voltage

Writing the dielectric constant $\varepsilon(\omega)$ of the material terms of its relative permittivity $\varepsilon'(\omega)$ and dielectric loss factor $\varepsilon''(\omega)$, i.e., $\varepsilon(\omega) = \varepsilon'(\omega) - j\varepsilon(\omega)$, and assuming that the dielectric material is linear so that the principle of super-position can be applied, it can be shown[10] that in the case of a step voltage applied at t = 0 to a conducting dielectric,

$$\varepsilon'(\omega) = \frac{1}{C_0} \left[C_\infty + \int_0^\infty \Phi(t) \cos \omega t \, dt \right] \qquad (1)$$

$$\varepsilon''(\omega) = \frac{1}{C_0} \left[\frac{G_0}{\omega} + \frac{1}{\varepsilon_0} \int_0^\infty \Phi(t) \sin \omega t \, dt \right] \qquad (2)$$

where C_∞ = capacitance of dielectric at very high frequencies, in farads,

$\quad C_0$ = capacitance of the system when sample is replaced by air, in farads,

$\quad G_0$ = steady-state d.c. conductance of the material, in ohm^{-1},

$\quad \Phi(t)$ = current decay function for the material, in amp volt^{-1},

$\quad \omega$ = angular frequency, $\omega = 2\pi f$, f is frequency in hertz.

The decay function $\emptyset(t)$ is obtained from the charging current $I(t)$ by the relationship

$$\emptyset(t) = \left(I(t) - I(\infty)\right)/V_o$$

where $I(\infty)$ is the final steady-state current (i.e., at $t \to \infty$) and V_o is the size of the step voltage applied.

For many dielectrics it is found that the decay function can be approximated over a wide range of values by

$$\emptyset(t) = KC_\infty t^{-n} \tag{3}$$

with K and n constants for a dielectric at any one temperature, and $n \sim 1$. The integrals (1) and (2) can then be evaluated to give

$$\varepsilon'(\omega) = \frac{C_\infty}{C_o}\left[1 + K\omega^{n-1}\ \Gamma\ (1-n)\cos\frac{(1-n)\pi}{2},\right]\ 0 < n < 1 \tag{4}$$

$$\varepsilon''(\omega) = \frac{1}{C_o}\left[\frac{G_o}{\omega} + KC_\infty\omega^{n-1}\Gamma\ (1-n)\cos\frac{n\pi}{2},\right]\ 0 < n < 2 \tag{5}$$

Eq. (5) for the dielectric loss factor can be greatly simplified[10] if $0.3 < n < 1.2$ when

$$\varepsilon''(\omega)\ \frac{I\ (0.63/\omega),}{\omega\ C_o V_o}\ \text{to within } \pm 3\% \tag{6}$$

or $\quad \varepsilon''(\omega)\ \dfrac{I\ (0.1/f),}{2\pi f\ C_o V_o}$, in terms of frequency $\tag{7}$

where $I(t)$ is the total current flowing in the material at time t. More importantly, this approximate result is still quite acceptable[9] even when the decay function departs considerably from the empirical expression, Eq. (3). Unfortunately, there is no equivalent simplification for the relative permittivity as the expression is not nearly so independent of the value of n. However, as $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are related to each other in a linear system, no new information is gained by the evaluation of the integral.

Hence, the dielectric loss factor at frequency f can be evaluated to a sufficient accuracy in terms of the total charging current at a time $t = 0.1/f$ sec after the application of a step voltage V_o to the sample. The method is independent

of C_∞, K, and n, and of the relative magnitudes of the decay current $V_0\phi(t)$ and conduction current V_0G_0, only the capacitance of the system in the absence of the dielectric being required to determine $\varepsilon''(\omega)$.

B. Ramp Voltage

The charging current in the case of a step voltage is dominated by a brief initial surge due to the instantaneous onset of the electronic and atomic polarization (broadened by the response time of the measuring system), which can be many orders of magnitude greater than the current due to the (low frequency) orientation polarization. This necessitates employing special techniques to by-pass the initial surge, and complicates the experimental details of the measuring circuits. This problem can be obviated by applying a ramp voltage $V(t) = V_0t/T$, $o \leqslant t \leqslant T$, to the sample in place of the step voltage. The resulting charging current $I(t)$ is given, from elementary circuit theory[12], assuming the sample to be a Debye dielectric with a parallel conducting path, by

$$I(t) = \frac{C_0V_0}{T}\left[\varepsilon_\infty + (\varepsilon - \varepsilon_\infty)\left(1-\exp(-t/\tau)\right)\right] + \frac{V_0t}{R_0T} \tag{8}$$

where ε_∞ = the high-frequency relative permittivity of the sample,

ε_S = the static (d.c.) relative permittivity of the sample,

τ = the single relaxation time of the sample (assumed to be a Debye dielectric) in seconds,

V_0 = the maximum voltage the ramp attains, t seconds after its application to the initially quiescent sample, in volts,

R_0 = the d.c. resistance of the sample, in ohms,

C_0 = the capacitance between the electrodes in the absence of any sample, in farads.

Clearly, the leading term within the square brackets in Eq. (8) $(C_0V_0 \varepsilon_\infty)/T$, can be made small in comparison with the initial surge in the step-voltage response, and the second term within the brackets is zero at t = 0 whereas the corresponding

one for the step-voltage response is not. Thus, large transients at very short times are no longer an experimental problem. However, correct identification of the leading term in Eq. (8) is still difficult, as it is somewhat modified by the response time of the measuring circuit.

This result can be readily generalized to the more realistic case of a non-Debye dielectric, now characterized by a distribution of relaxation times rather than the unique relaxation time of a perfect Debye dielectric. This distribution function is defined by[11]

$$\Phi(t) = \int_0^\infty f(\tau)\exp(-t/\tau)d\tau, \text{ with } \int_0^\infty f(\tau)d\tau = 1$$

where $\Phi(t)$ is the decay function of the sample. The fitting of the observed currents to the generalized result is difficult, however, and requires extensive computation. For many systems the difference between the observed current and that given by Eq. (8) is small, and only a slight error is made in analyzing the behavior via this equation, at a considerable saving of time and effort.

The expected response of a Debye dielectric with parallel conducting path is shown in Fig. 1. The response is in three parts. For very short times the response is dominated by the initial term in Eq. (6), modified slightly by the finite response time of the circuit. Shortly thereafter, the exponential charging of the dielectric takes over and one observes a slowly increasing rise in the charging current. At very long times, however, the current does not saturate, but continues to rise linearly with time due to the parallel conduction current. Examination of Eq. (8) and Fig. 1 shows that the initial current $I(o) = (C_0V_0\varepsilon_\infty)/T = A$ and that the linear region at times approaching T extrapolates back to give an intercept $(C_0V_0 \varepsilon_s)/T = B$, at $t = 0$, and a slope V_0/R_0T, from which the bulk d.c. resistance R_0 of the sample may be estimated. The difference between $I(t)$ and the (extrapolated) linear region is

$$I(t) = (\varepsilon_s - \varepsilon_\infty) \frac{C_0V_0}{T}\exp (-t/\tau) \qquad (9)$$

When plotted on log-linear coordinates Eq. (9) yields a value for τ from the slope

of the resulting straight line. The quotient A/B gives the ratio of the static, relative permittivity for the sample, $\varepsilon_s/\varepsilon_\infty$. The method can be checked by observing the degree to which the current obeys Eq. (9), and also by plotting A versus V_o/T and B versus V_o/T for various values of V_o and T. A linear dielectric should yield straight lines for these two expressions.

IV. RESULTS AND DISCUSSION

A. Step Voltage

The response of the sample to step-voltage waveforms was measured at room temperature (295 K) and at $119^\circ C$ (392 K), for various voltage amplitudes between 0.7 and 30 volts. Figure 2 shows a result for T = 295 K and V_o = 10 volts, and is typical of the response found in BCPMA for all the voltages used at both temperatures. An initial surge current, whose peak values is in excess of 100 pA appears for t < 1 sec, followed immediately by a decay of the current, initially quite precipitous, later (t > 50 sec) much more leisurely, to a final steady value I_s = 7.5 pA found at $t > 10^4$ sec. Using this value of I_s, the decay function $\Phi(t)$ can be obtained from Fig. 2 as $\Phi(t) = \left(I(t) - I_s\right)\!\Big/\!V_o$.

A plot of log $\Phi(t)$ versus log t is shown in Fig. 3, and corresponds to the data of Fig. 2. As can be seen, for 2 < t < 1000 sec the decay function for BCPMA can be accurately expressed as a simple power of the time. In this example $\Phi(t) = 2.6/t^{0.59}$ pA volt^{-1}. The value of n, 0.59, is within the limits (0.3 - 1.2) set by Harmon for the acceptable use of his approximate expression for the dielectric loss factor[11]. Similar values of n were found for the other voltages used, and also at the higher temperature. Consequently, the dielectric loss factor $\varepsilon''(f)$ can be found for BCPMA by simple application of Eq. (7) to the sample response curves I(t) versus t.

Only the frequency variation of ε'', however, was determined in the present study as the irregular shape of the samples does not permit an accurate value for C_o to be obtained. An order of magnitude estimate of C_o (from sample dimensions)

would be about 10^{-1} pF. The results are shown in Fig. 4. Clearly, to within the experimental error, the results are independent of the applied voltage, as indeed they must be if the system is a linear dielectric. The dielectric loss factor at the higher temperature is approximately 16 times larger than at room temperature. The most unusual result, though, is the frequency dependence of ε''. At both temperatures, ε'' increases rapidly with decreasing frequency, and shows no indications of leveling off and saturating. Although a certain amount of curvature can be seen in the dependence of log ε'' on log f, to a satisfactory accuracy, in the frequency range 10^{-4} to 10^{-1} Hz $\varepsilon''(f) = (A\ f^{-0.9})/C_O$ with A = 0.32 pF Hz^{-1} at 295 K and 4.17 pF Hz^{-1} at 392 K.

This particular dependence of ε'' on an inverse power of the frequency implies from the Kamers-Kronig relationship[10] between ε' and ε''

$$\varepsilon'(\omega) - \varepsilon'(\infty) = \frac{2}{\pi} \int_0^\infty \frac{u\varepsilon''(\omega)}{u^2 - \omega^2}\ du$$

that $\varepsilon'(\omega)$ will also be strongly dependent on frequency in this region, essentially given by $\varepsilon'(\omega) = \varepsilon'(\infty) + 1/\omega^m$ to first order in some logarithm of $\boldsymbol{\omega}$ and where m is approximately unity.

$\varepsilon'(\omega)$ has been previously reported[8] to vary approximately as $\omega^{-0.75}$ at room temperature in the frequency range 10^{-3} to 1 Hz, with similar variations indicated for temperatures between 77 and 400 K. These values were deduced from the variation of sample capacitance with frequency, measured using a.c. detection techniques. The present results confirm this unusual behavior.

Experimental evidence, therefore, indicates that BCPMA enjoys an unusual increase in its dielectric constant as frequencies approach d.c. conditions. This behavior is quite similar to that found in a wide variety of solid dielectrics.[7]

B. Ramp Voltage

The response of the samples to ramp-voltage waveforms could only be accurately measured at room temperature, the conduction current overwhelming the dielectric charging current at the higher temperature (392 K) due to the much smaller sample

resistance involved (< 10^9 ohm at 392 K compared to ~10^{12} ohm at 300 K). This three order of magnitude increase in conduction current is far in excess of the one-order increase expected in ε_s due to the temperature increase and hence the dielectric charging current, $C_oV_o \varepsilon_s/T$. Various maximum voltage amplitudes V_o between 0.4 and 32 volts were employed.

Figure 5 shows a typical response of a sample of BCPMA to a ramp waveform $V(t) = 0.16 t$ (i.e., 30 volts applied linearly over a time T = 190 sec). It is quote similar to the theoretical expression graphed in Fig. 1, with two important exceptions.

Firstly, the initial current step $I(o) = (C_oV_o\varepsilon_\infty)/T$ is absent, or rather, too small to register on the current scale employed, 0.94 pA cm^{-1}. This would indeed be expected if an anomalous dielectric relaxation process were present in BCPMA at very low frequencies as then $\varepsilon_s/\varepsilon_\infty >> 1$ and the charging current $(C_oV_o \varepsilon_s)/T$ would be many times larger than the initial current step $(C_oV_o \varepsilon_\infty)/T$. That the initial current step $I(o)$ is absent, and not merely masked by the measurement system risetime, can be seen when the risetime of the current response for $0 < t < 2$ sec is evaluated. Risetimes (for all voltages employed) were of the order of 1 sec. The system risetime (for step-voltage waveforms) was measured at less than 3×10^{-2} sec, at least one, sometimes two orders of magnitude smaller than the current risetimes observed.

Secondly, the charging current was found to be approximately characterized by two risetimes, τ_1 and τ_2, with $\tau_2 \sim 10\tau_1$, indicating that the sample, as to be expected, was not a perfect Debye dielectric. Even so, the simple theory is still valid for $t \rightarrow 0$ and $t \rightarrow \infty$, with intercept at $t = 0$ still given by $(C_oV_o \varepsilon_s)/T$ and the slope of the linear region by V_o/R_oT.

The sample risetimes were obtained by plotting $i(t)$, the difference between the response current and the extrapolated linear region, against time on semi-logarithmic coordinates. The result for the response displayed in Fig. 5 is shown

in Fig. 6 (circles). For $0 < t < 20$ sec $i(t)$ can be well fitted to the expression

$i(t) = 4.72 \exp (-3.03 t) + 2.74 \exp (-0.20 t)$ pA

giving $\tau_1 = 0.33$ sec and $\tau_2 \sim 10_{\tau 1} = 4.98$ sec, and a final charging current $(C_0 V_0 \varepsilon_s)/T = 7.46$ pA. As expected, the intercept B of the linear region depends linearly on applied voltage V_0 (Fig. 7). With C_0 approximately 10^{-1} pF and T = 190 sec, the experimental value of the slope of the line in Fig. 7, when equated to $C_0 \varepsilon_s/T$, gives an estimate $\varepsilon_s \simeq 500$, a rather large value for the static dielectric constant of a material, but one consistent with the values found by Pohl and coworkers in other polymeric systems[4-6], and reported in other solid dielectric too.[7] This high value for ε_s ensures that the ratio $\varepsilon_s/\varepsilon_\infty >> 1$ as $\varepsilon_\infty \sim 1$ in most materials. It is therefore not surprising that the current step $A = C_0 V_0 \varepsilon_\infty/T$ is absent in the response of BCPMA to ramp waveforms.

The risetimes τ_1 and τ_2 of the material were also found to be voltage dependent (Fig. 8), both seemingly varying as $V_0^{-\frac{1}{4}}$, to within the admittedly large experimental error. The data scatter is so much larger in the case of τ_1 than τ_2 because the current associated with τ_1 only dominates in the total charging current for such a brief time (<3 sec) before it is masked by the current associated with τ_2. Estimating risetimes from time bases as short as 2-3 sec results in these large errors.

Finally, the slope of the linear region of the current response (Fig. 5) enables an estimate of the bulk resistance of the sample to be made. Remarkably uniform values for R_0 were obtained, considering the large differences in the values of V_0 and T used in each case.

Setting $R_0 = V_0/I$ and plotting $\log V_0$ versus $\log I$, these data can be displayed as in Fig. 9 (solid points). The data fall quite close to an ohmic line, with a resistance of 6.5×10^{11} ohm. The full triangles represent the bulk resistance of the sample measured using normal d.c. potentiometric techniques. The agreement is quite acceptable.

The curvature seen in the behavior of these latter data, especially at very low d.c. voltages (<100 mV) is probably due to both the great difficulty in arriving at the true steady-state conduction current of the sample in finite measuring times (t < several days), because of the extremely slow decay of the polarization current, and also the limiting ability of the measuring circuit to detect such extremely small currents. The currents finally recorded in these cases were probably still in excess of the true d.c. current.

The behavior of the low-frequency dielectric loss in BCPMA (Fig. 4) is thus quite typical of a large class of solid dielectrics where the dielectric loss increases with decreasing frequency as ω^{-m} and shows no sign of low frequency saturation or decrease to zero as required by the Debye model. While this behavior would seem to be due to the discontinuous hopping of charged carriers in many materials--especially electrons in amorphous semiconductors, the models advanced for most systems are ad hoc in nature and quite arbitrary, being typically distributions of Debye relaxation processes but needing unphysically large ranges of relaxation time. The very universitality of this dielectric response has led Jonscher[7] to suggest that only an extremely general mechanism, interest in all dielectrics, is responsible for the observed common behavior. He proposes that the screening of charges and dipoles as a result of many-body interactions is the required general mechanism and has developed a screened-hopping model based on many-body formalism. Qualitative agreement with observation is obtained. Give the lack of precise quantitative models, the low frequency dielectric behavior of BCPMA is compatible with the hopping of charged carriers between random localized centers, and is clearly due to the same underlying 'universal' response postulated by Jonscher.

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The author to whom correspondence should be addressed at the Department of Physics.

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CAPTIONS FOR FIGURES

Figure 1.   Response of a Debye dielectric with parallel conduction path to a ramp waveform (Eq. 6 with $\varepsilon_0 = 3\varepsilon_\infty$, $\tau = 0.16T$, and conduction current = dielectric current at $t = T$). $I(t)$ in arbitrary units.

Figure 2. $I(t)$ versus time for BCPMA at $T = 295$ K subjected to a step waveform, magnitude 10 volts. $I(\infty) = 7.5$ pA @ $t > 10^4$ sec. $I(t) > 100$ pA @ $t < 1$ sec.

Figure 3.   Log $\Phi(t)$ versus time: the experimental points are from Fig. 2, the line represents best fit to the power law $\Phi(t) = 26t^{-0.59}$ pA volt^{-1}.

Figure 4.   Log $\varepsilon''C_0$ versus log f for various step voltages applied at $T = 392$ K and $T = 295$ K.

Figure 5. $I(t)$ versus time for BCPMA at 295 K subjected to a ramp waveform $V(t) = 0.16t$ (i.e., 30 volts peak at $T = 190$ sec).

Figure 6.   Log $i(t)$ versus time: the experimental points are from Fig. 5, the line represents the best fit to the double exponential expression $i(t) = 4.7e^{-3.0t} + 2.7e^{-0.2t}$ pA.

Figure 7.   Dependence of the intercept B on voltage V. Theoretical slope given by $C_0 \varepsilon_s/T$, experimental slope 0.26 pA/volt giving ε_s 500 for $T = 190$ sec and C_0 10^{-1} pF.

Figure 8.   Log τ_1 and log τ_2 versus log V_0. Lines are of the form $\tau = AV_0^{-\frac{1}{4}}$ with $A = 11.3$ (upper, τ_2) and 0.95 sec (lower, τ_1).

Figure 9.   Log V_0 versus log I at $T = 295$ K for: a) d.c. potentiometric measurements (full triangles) and b) values of I obtained from $I = V_0/R_0$ (full circles) with R_0 given by the slope of linear conduction region in sample response to a ramp waveform, slope $= V_0/R_0T$. Ohmic dependence, $R = 6.5 \times 10^{11}$ Ω.
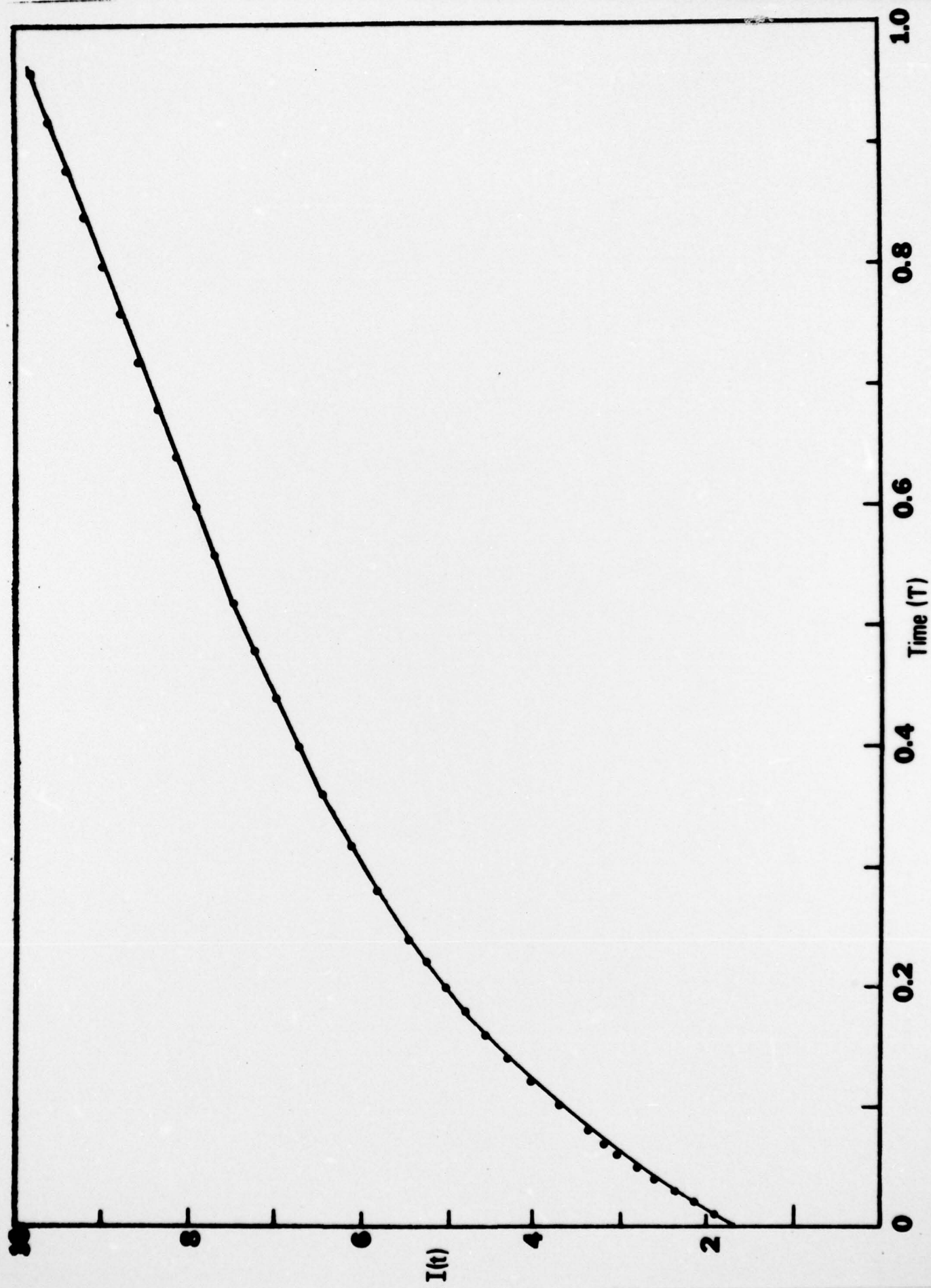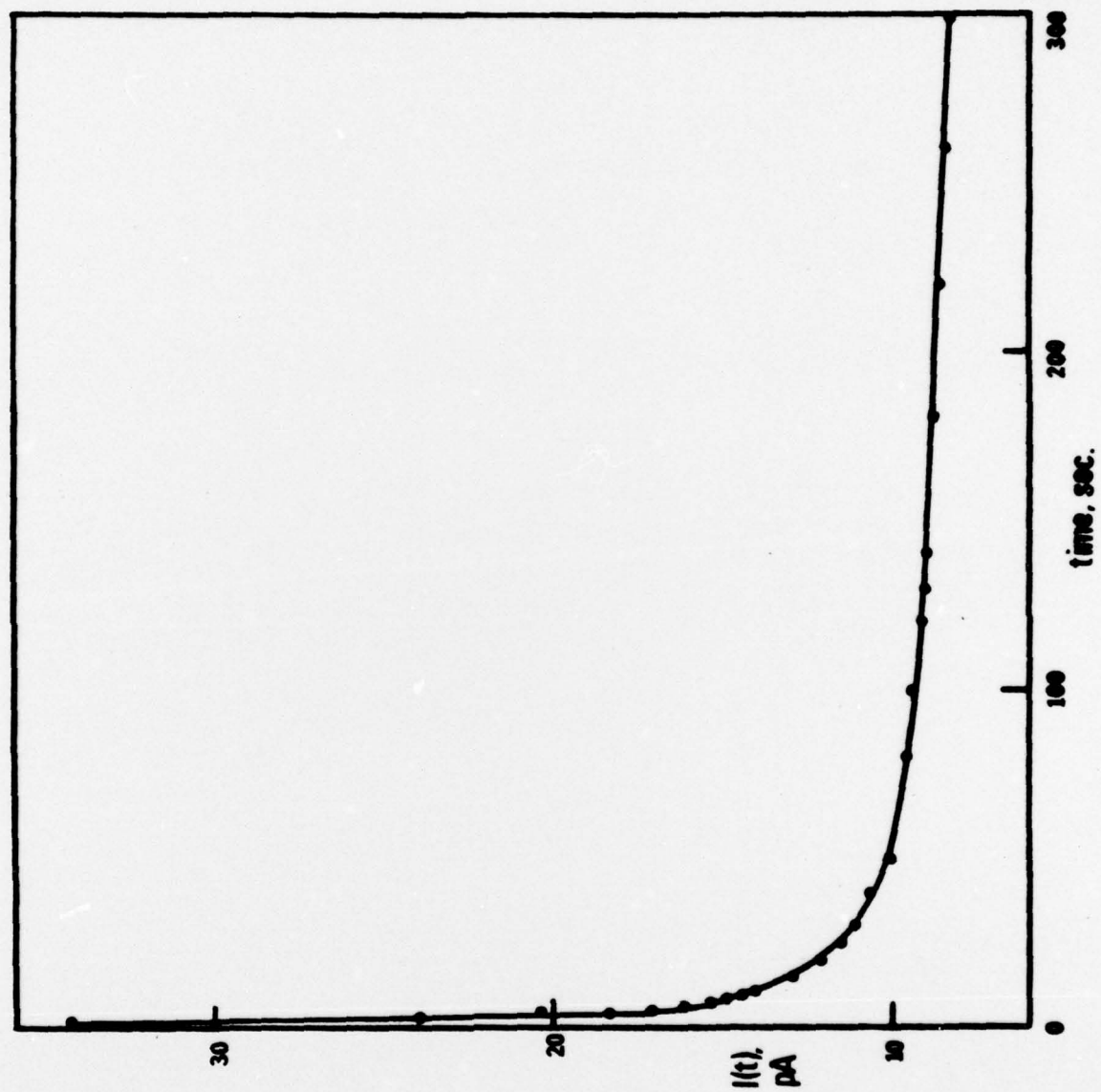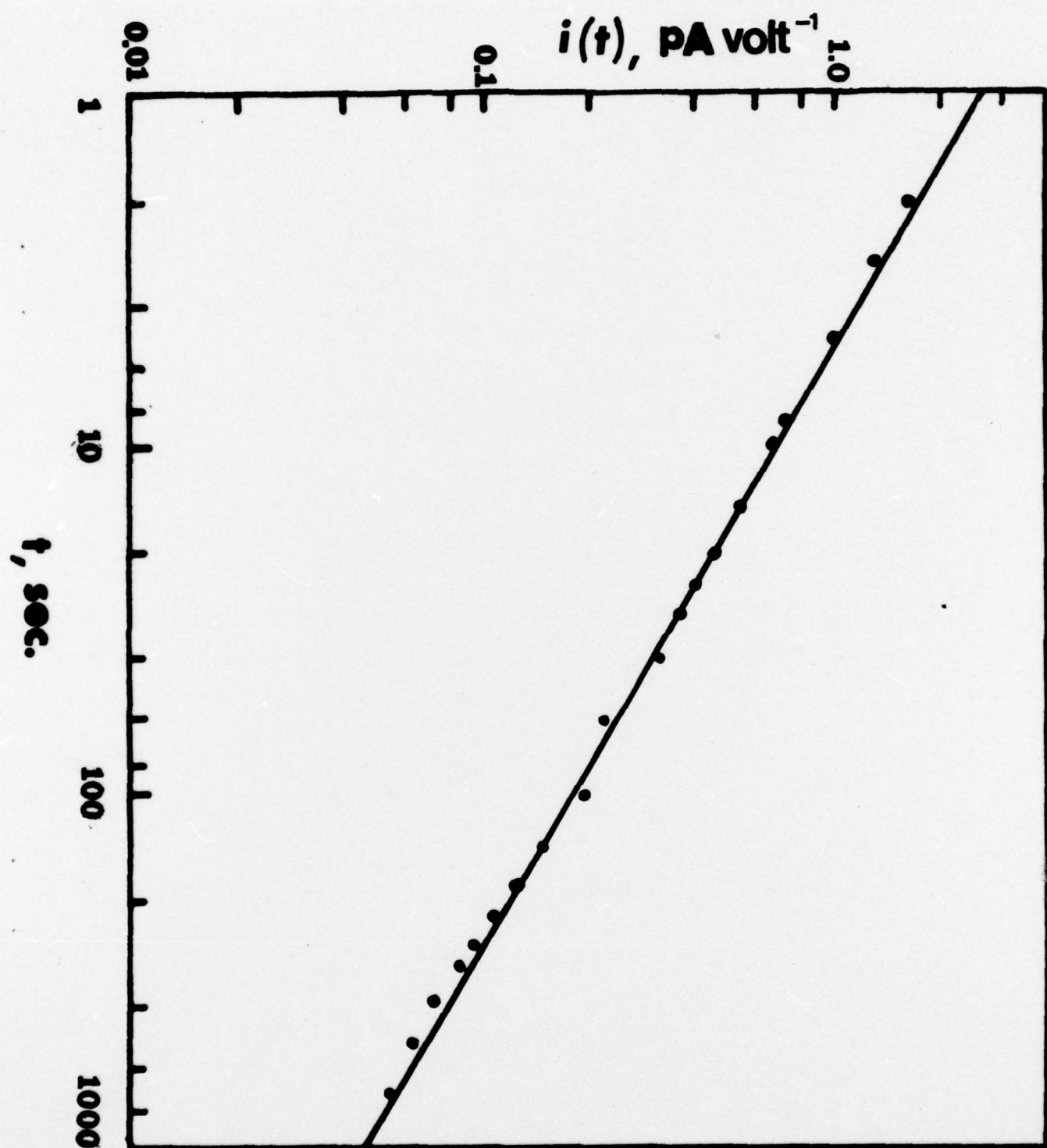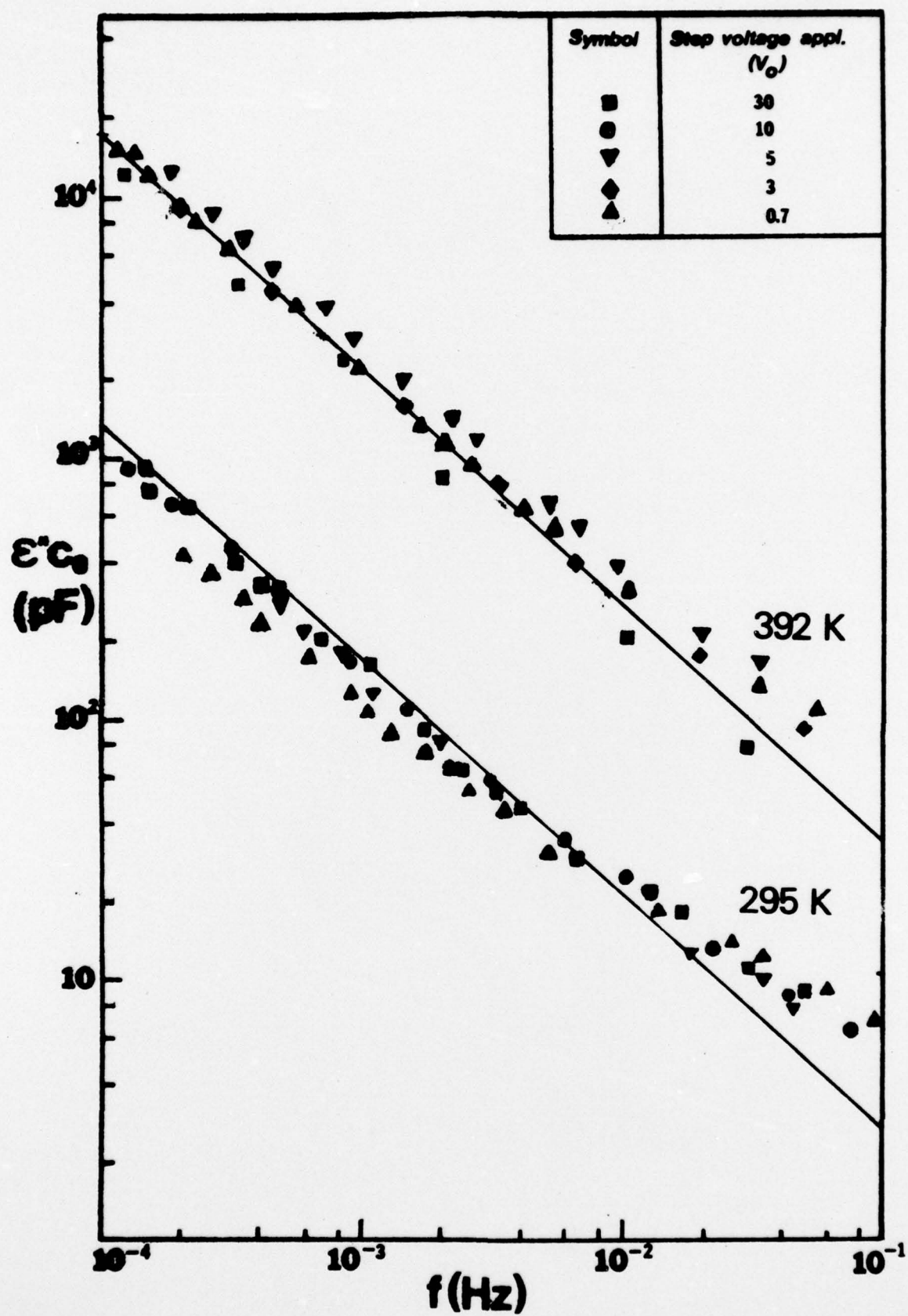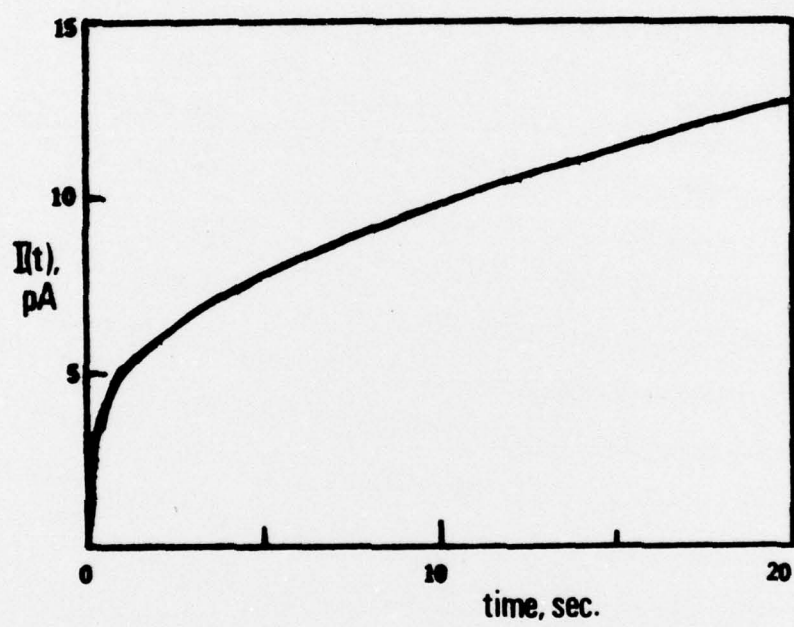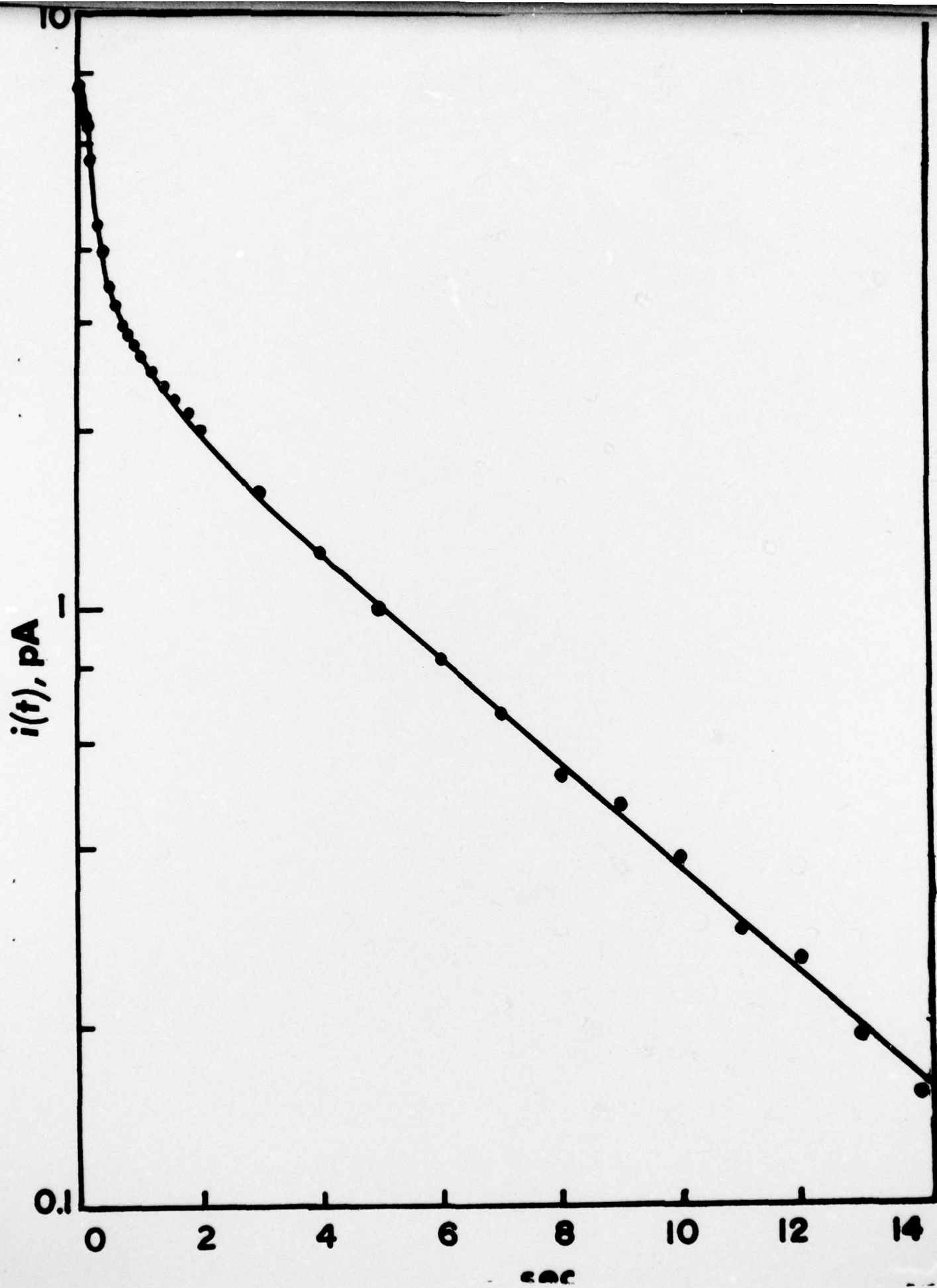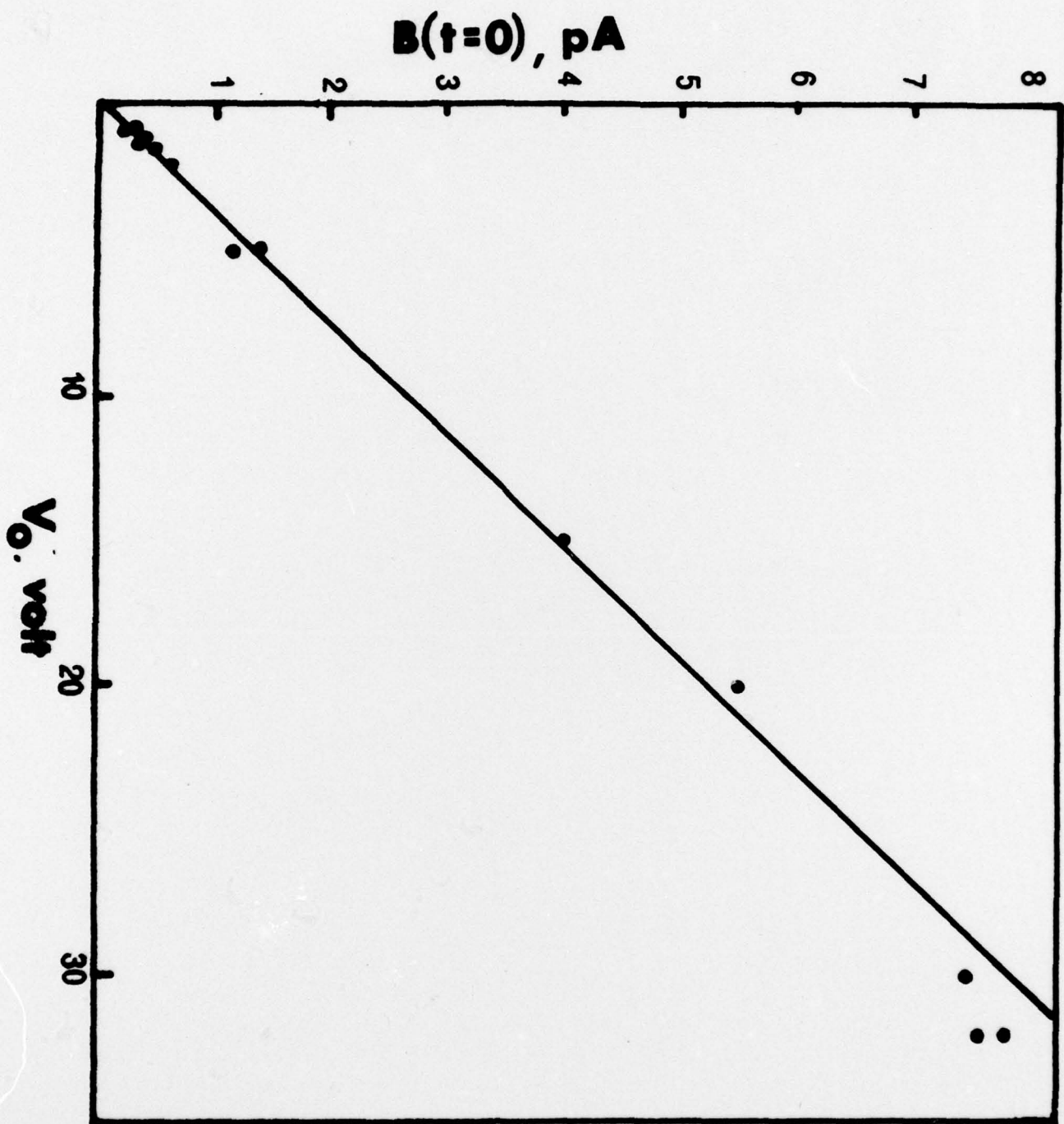
FIG.4

FIG.5

FIG. 7

FIG. 8

T = 295 K

Fig. 9
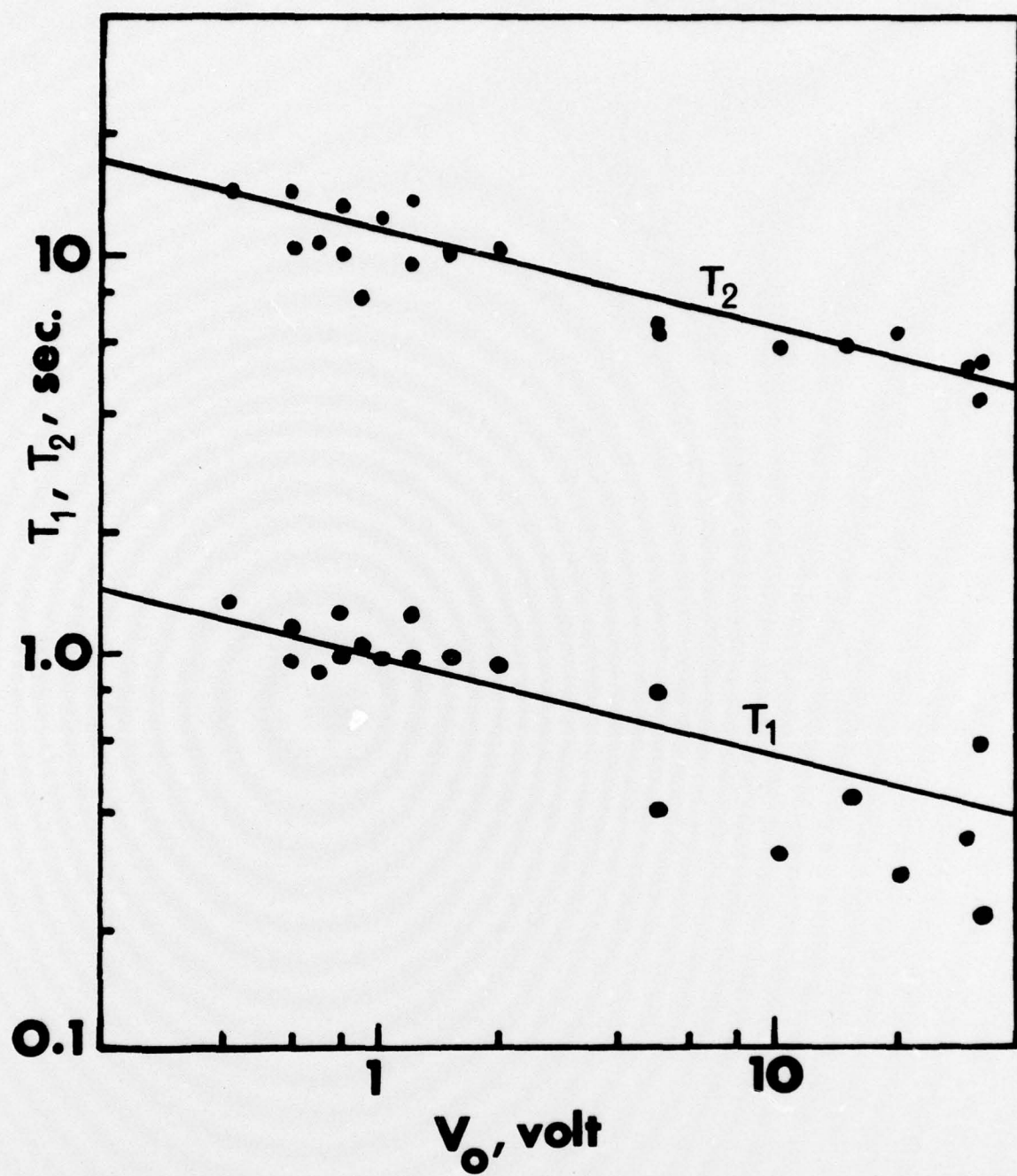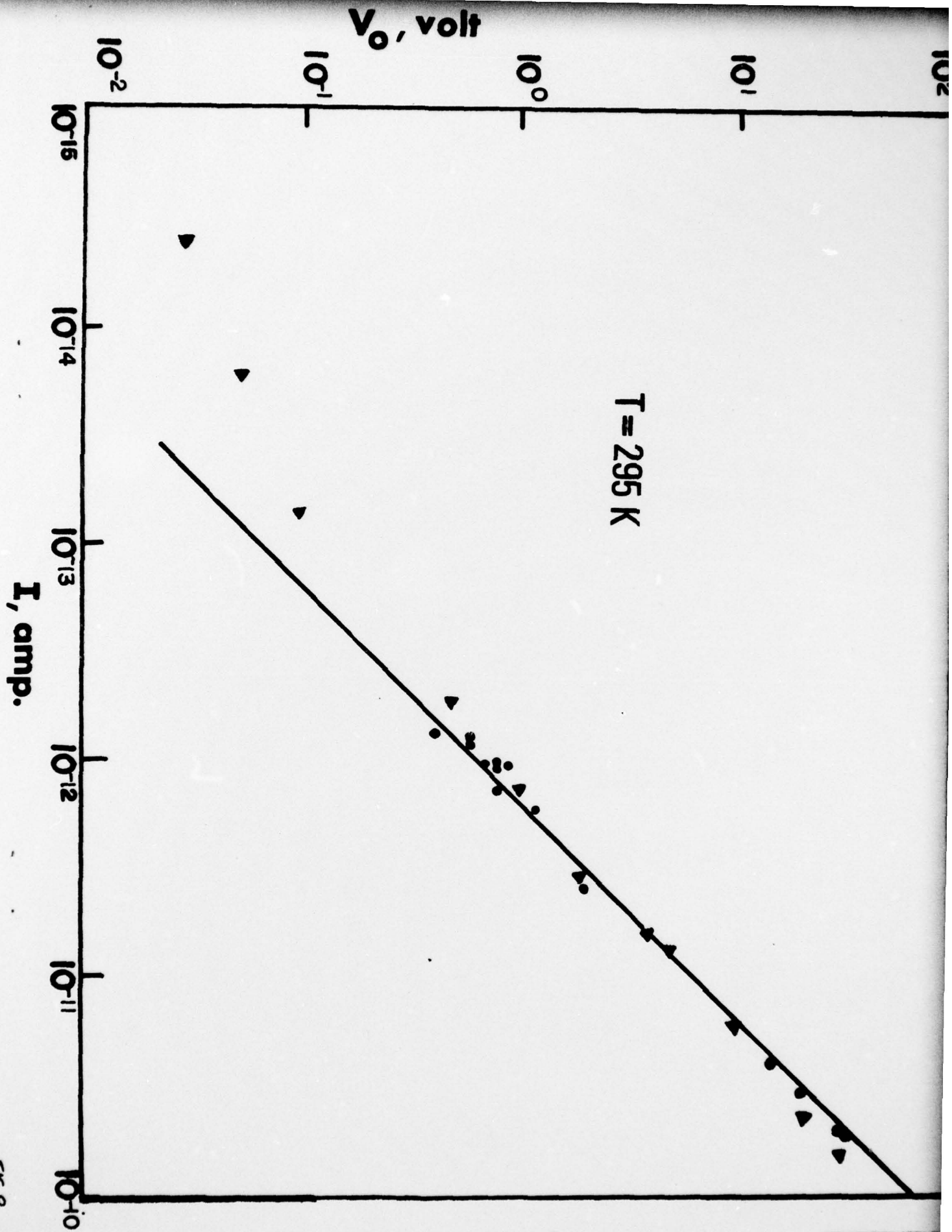
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